

5/14/99



Office of Prevention, Pesticides,
and Toxic Substances

SUBJECT: Use of Pyridate (PC # 128834) on mint in Indiana State
Environmental Fate and Effects Division
Bar Code: D254808

FROM: Fred Jenkins, Aquatic Biologist
Environmental Risk Branch 2
Environmental Fate and Effects Division (7507C)

Fred Jenkins 5/14/99

THROUGH: Pat Jennings, Acting Chief
Environmental Risk Branch 2
Environmental Fate and Effects Division (7507C)

Pat Jennings 5/14/99

TO: Barbara Madden (7505C)
Registration Division

Attached to this memo is the requested Section 18 for Pyridate use on mint in Indiana State (DP Bar Code: D254808). If there are any questions, please contact Fred Jenkins at (703) 308-9597.



Section 18 Review
Use of Pyridate (PC # 128834) on mint in Indiana
Environmental Fate and Effects Division
Bar Code: D254808

I. Summary:

The level of concern for acute risk of pyridate is not expected to be exceeded for birds and mammals (including endangered species). The level of concern has been exceeded for chronic risk to mammals (including endangered species; see sec. V & sec. VI). Freshwater, marine, and estuarine fish and invertebrates (including endangered species) are not expected to be adversely affected by the proposed use. Since there are no plant toxicity data available, no plant risk assessment can be done. Therefore, EFED assumes that terrestrial and aquatic non-target plants (including endangered species) may be adversely affected from the labeled use of pyridate. Potentially exposed endangered plant species are listed in sec VI. Measures must be taken to ensure the protection of these species from pyridate exposure by contacting Indiana state endangered species program and/or the U.S. Fish and Wildlife Service.

The proposed use is not expected to pose significant risk to surface and ground water resources. For surface water, the maximum expected concentrations are 97 $\mu\text{g/L}$ for acute risk calculations and 75 $\mu\text{g/L}$ for chronic risk and cancer risk calculations. Concentrations in ground water are not expected to exceed 4.44 $\mu\text{g/L}$. Modifications of label statements are not recommended.

II. Background

The Indiana State Department of Agriculture is requesting an Emergency Exemption for the use of pyridate to control broadleaf weeds on mint. This exemption is for the use of Tough 5.0 EC herbicide[®] (Registration # 100-877), containing 55.8% of active ingredient of pyridate. This exemption would allow use during May 1 through December 31, 1999 in the counties of Stark, LaPorta, Jasper, St. Joseph, LaGrange, Pulaski, Kosciusko, Newton, and Porter. A total of 9,200 acres may be treated.

Application Rate: 0.9375
No. of Applications: 2
Application Method: Ground

For general use, the maximum application rate for pyridate on any crop is 0.9375 lb. ai/A for mint.

III. Environmental Fate Summary

Pyridate hydrolyzes rapidly with half lives of 66.7, 17.8, and 6.8 hours at pH 5, 7, and 9, respectively. The degradate, CL-9673, appears to be stable to hydrolysis with a reported half life of >35 days (>95% remained as CL-9673 after 35 days) (See Attached memo: Section 18 Emergency Exemption - Use of Pyridate on Garbanzo Beans (Chickpeas) in Washington State to Control Broadleaf Weeds: D244668, PC Code# 128834, ID # 98WA0031).

Pyridate does not undergo any significant aqueous or soil photolysis, but is rapidly hydrolyzed to CL-9673, which is in turn readily photolyzed in water with a half life of 3.7 to 14 days and on soil with a half life of 16 days. These half lives indicate that pyridate and its primary degradate will be short lived in the environment when exposed to sunlight. CL-9673 has terrestrial field dissipation half lives ranging from 7-29 days.

In anaerobic conditions, the degradate is persistent with a half life for anaerobic soil metabolism of 330-630 days. The soil partition coefficient (K_d) for CL-9673 is 0.3-3.5, indicating it is not sorbed.

Neither pyridate nor CL-9673 is volatile, with a vapor pressure for pyridate of 7.49×10^{-9} , and a Henry's Constant of 2.49×10^{-9} , meaning pyridate is less volatile than water. A fish study indicated that pyridate bioaccumulates (464 times), but 99% of residues were eliminated in 14 days.

In summary, the data indicate that in terrestrial and aquatic environments, pyridate rapidly hydrolyzes to CL-9673 with half lives usually ≤ 3 days. Although pyridate is also rapidly hydrolyzed under anaerobic soil conditions to CL-9673, CL-9673 is persistent and undergoes very little degradation with half lives from 330-630 days in anaerobic soil conditions. Aerobic half lives of CL-9673 are about 10-30 weeks in soils (incorrectly given as 10-30 days in the EPA one-liner database). CL-9673 is rapidly degraded under the influence of light as indicated by the 14 day half life in the water and 16 day half life in soil. In general, pyridate and its primary degradate, CL-9673, will not persist in aerobic conditions, while CL-9673 will persist in anaerobic conditions.

IV. Water Resources Summary

A. Surface Water (Modeling and Monitoring)

It is EFED's understanding that the Garbanzo use is the highest registered use rate for pyridate. Since the application rate and frequency of application is the same for both of the garbanzo use and mint use, the estimated surface water drinking water and ecological exposure are the same for both uses.

The GENEEC model was used to estimate surface water concentrations for pyridate (See Attached Memo: Pyridate Environmental Fate Characteristics and Estimated Ground Water and Surface Water Concentrations Resulting from Proposed Use on Garbanzo Beans: Chemical No. 128834, DP Barcode D223398, Case 287340, ID 6E04667). The modeling results show that pyridate has the potential to move into surface waters, especially during times of unusually heavy rainfall.

The peak GENEEC estimated environmental concentration (EEC) of pyridate in surface water is 97 ppb (Table 1). This estimate is based on a maximum application rate of 0.9 lb. ai/acre. The GENEEC values represent upper-bound estimates of the concentrations that might be found in surface water due to pyridate use.

Available data show that pyridate and its primary degradate degrade rapidly by hydrolyses and photolysis and would not be expected to create a surface water contamination problem. However, if runoff were rapid, taking less time than the aqueous photolysis half life of up to 14 days, such as following a heavy rain, and CL-9673 was discharged to surface water with anaerobic conditions, it then could persist for a significant length of time of 1.5 to 2.5 years. (An anaerobic aquatic half life is not known, but can be estimated from the anaerobic soil metabolism value to be 1.5 to 2.5 years).

GENEEC (US EPA, 1995) is a screening model designed by the Environmental Fate and Effects Division (EFED) to estimate the concentrations found in surface water for use in ecological risk assessment. As such, it provides upper-bound values on the concentrations that might be found in ecologically sensitive environments because of the use of a pesticide. It was designed to be simple to use and to only require data that is typically available early in the pesticide registration process. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC is hardwired to represent a 10-hectare field immediately adjacent to a 1-hectare pond that is 2 meters deep with no outlet. The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 10% of the applied pesticide into the pond. This amount can be reduced due to degradation on the field and the effects of soil binding in the field. Spray drift is equal to 1 and 5% of the applied rate for ground and aerial spray application, respectively.

1) Aquatic Ecosystems

Table 1. Tier I upper tenth percentile EEC's for pyridate.

Compound	Peak GEEC	4 Day GEEC	21 Day GEEC	56 Day GEEC
Garbanzo beans	97 ppb	95 ppb	88 ppb	75 ppb

Input values used in the surface water model are given in Table 2.

Table 2. Surface Water Exposure Inputs for GENEEC for Pyridate.

DATA	VALUE
Application rate	0.9 lbs. ai/A (label)
Maximum number of application per year	2 (label)
Interval between applications	20 days (label)
Soil organic carbon coefficient (Koc)	3 (lowest computed for three soils) ¹
Soil aerobic metabolism (maximum value)	210 days
Solubility	1.5 ppm (one liner database)
Aerobic aquatic metabolism half life	75 days(one liner, supplemental study)
Photolysis half life	14.1 days

2) Drinking Water

EFED recommends that the same concentrations derived for the surface water be used for the drinking water assessment (See attached memo: Pyridate Environmental Fate Characteristics and Estimated Ground Water and Surface Water Concentrations Resulting from Proposed Use on Garbanzo Beans: Chemical No. 128834, DP Barcode D223398, Case 287340, ID 6E04667).

EFED recommends a peak EEC of 97 ug/L for the acute human health risk assessment from surface water source drinking water. The EEC that should be used for the chronic and cancer human health risk assessments from surface water source drinking water is the 56 day mean value of 75 ug/L. The EEC is based on the use rate of 0.09 lbs/acre. It is EFED's understanding that 0.09 lbs/acre is the highest registered use rate.

3) Monitoring

No monitoring data are available at this time.

B. Ground Water

Table 3 shows the input parameter values used in SCI-GROW for pyridate and the resulting estimated ground water concentration.

EFED estimates a ground water drinking water exposure concentration of 4.44 ppb for pyridate as predicted by SCI-GROW modeling results (See attached memo: Pyridate Environmental Fate Characteristics and Estimated Ground Water and Surface Water Concentrations Resulting from Proposed Use on Garbanzo Beans: Chemical No. 128834, DP Barcode D223398, Case 287340, ID 6E04667). There may be exceptional circumstances under which groundwater concentrations could exceed the SCI-GROW estimates. However, such exceptions should be quite rare since the SCI-GROW model is based exclusively on maximum groundwater concentrations from studies conducted at sites and under conditions which are most likely to result in groundwater contamination. The groundwater concentrations generated by SCI-GROW are based on the largest 90-day average recorded during the sampling period. The concentration (4.44 ppb) can be considered as both the acute and chronic values.

Table 3. SCI-GROW Environmental Fate Input Parameters for Pyridate

Average K_{oc} (l/kg) ¹	64.5
Application rate (lb a.i./acre)	0.9
Number of applications per year	2
Use rate (maximum total/season)	1.8 lb ai/A
Aerobic soil metabolism half-life (days)(average)	105
Relative intrinsic leaching potential	4.9
Estimated groundwater concentration	4.44 ppb

C. Recommendations for Drinking Water Concentrations

EFED recommends a peak EEC of 97 ug/L for the acute human health risk assessment from surface water source drinking water. The EEC that should be used for the chronic and cancer human health risk assessments from surface water source drinking water is the 56 day mean value of 75 ug/L. The EEC is based on the use rate of 0.09 lbs/acre. It is EFED's understanding that 0.09 lbs/acre is the highest registered use rate.

V. Ecological Risk Assessment

A. Terrestrial Animals

Risk quotients indicate that the level of concern (LOC) for acute risk for the proposed use is not exceeded for terrestrial animals (Table 3). Risk quotients also indicate that the LOC for chronic risk is not exceeded for birds, but the LOC for chronic risk is exceeded for mammals (Table 4). EFED has determined the chronic risk may primarily affect small vegetarian mammals. Small vegetarian mammals could possibly be exposed directly to pyridate because of their dietary behavior.

Table 4. Toxicity and Risk Quotients for Terrestrial Wildlife [and Beneficial Insects].

Animal Group	Exposure Type	Most Sensitive Species	Toxicity	EEC (ppm)	Risk Quotient
Birds	Acute	Northern bobwhite and Mallard	LC ₅₀ = 1505 ppm ^a	432 ^b	< 0.1 ^c
Birds	Chronic	Northern bobwhite and Mallard	NOAEL= 640 ppm ^a	432	< 1 ^c
Mammals	Acute	Rat / Mouse	LD ₅₀ =3544 mg/kg ^a	432	< 0.1 ^c
Mammals	Chronic	Rat / Mouse	NOAEL= 216 ppm ^a	432	2 ^d
Insects	Acute	Honeybee	No Record	NA	NA

^a Sec 18 DP Barcode D244668

^b The exposure for terrestrial animals is usually determined by the Kenaga/Fletcher nomogram. The highest terrestrial residue anticipated is determined by multiplying the residues found on short grass (240 ppm) after application of 1 lb ai/A with the application rate (0.9 x 2 applications) resulting in 432 ppm.

^c The risk quotient does not exceed any level of concern.

^d The risk quotient exceeds the level of concern for chronic risk to mammals.

B. Aquatic Animals

The level of concern (LOC) is exceeded for endangered freshwater fish. Since there are no endangered freshwater fish in Indiana, there is no concern for endangered freshwater fish in Indiana (Table 5).

The level of concern (LOC) is exceeded for marine and estuarine fish. However, there are no marine or estuarine fish in Indiana. Therefore, there is no concern for marine or estuarine fish.

The LOCs for estuarine and marine invertebrates is exceeded. There are no marine and estuarine invertebrates in the state of Indiana. Therefore, there is no concern for marine and estuarine invertebrates in Indiana.

However, there are endangered freshwater invertebrates in Indiana. The level of concern is exceeded for endangered freshwater species of invertebrates in Indiana (See Endangered Species Sec VI).

There are no chronic data available to provide chronic risk assessment for aquatic species.

Table 5. Toxicity and Risk Quotients for Aquatic Animals.

Animal Group	Exposure Type	Most Sensitive Species	Toxicity	EEC (ppb)	Risk Quotient
Freshwater Fish	Acute	Freshwater fish	LC ₅₀ = > 1200 ppb ^a	97 ^b	0.08 ^c
	Chronic	Fathead minnow	No Record		
Freshwater Invertebrates	Acute	<i>Daphnia magna</i>	LC ₅₀ = 1080 ppb ^a	97	0.09 ^c
	Chronic	<i>Daphnia magna</i>	No Record		
Estuarine/ Marine Fish	Acute	Sheepshead minnow/ Silverside	LC ₅₀ 300 ppb ^a	97	0.32 ^d
	Chronic	Sheepshead minnow	No Record		
Estuarine/ Marine Invertebrates	Acute	Eastern oyster	LC ₅₀ = 145 ppb ^a	97	0.66 ^e
	Chronic	Mysid	No Record		

^a Sec 18 DP Barcode D244668^b Derived by GENEEC Model.^c The level of concern has been exceeded for endangered species.^d The level of concern has been exceeded for acute restricted use.^e The level of concern has been exceeded for acute high risk.

C. Terrestrial and Aquatic Plants

Since there are no plant toxicity data available, no plant risk assessment can be done. Therefore, a default assumption is that terrestrial and aquatic non-target plants (including endangered species) may be adversely affected from the labeled use of pyridate.

VI. Effects on Endangered Species

The level of concern (LOC) is exceeded for endangered freshwater fish. However, there are no endangered freshwater fish in Indiana. Therefore, there is no concern for endangered freshwater fish in Indiana (Table 5).

The level of concern is exceeded for endangered freshwater invertebrate species (Table 5).

The following endangered freshwater invertebrate species may inhabit the following counties where pyridate is to be used:

<u>County</u>	<u>Species</u>
Pulaski	Tubercled-blossom Pearlymussel
Kosciusko	Clubshell Clam Tubercled-blossom Pearlymussel

The LOC for endangered species of freshwater invertebrate is exceeded (See table 5). EFED has determined that the endangered invertebrate will not be affected by the proposed use of pyridate because the endangered invertebrate species inhabit rapidly flowing rivers and streams, and are not indigenous to the farms ponds on which the estimated environmental concentration modeling results are based. Therefore, exposure of these invertebrate species to pyridate is not expected to warrant any concern.

Although the LOC is exceeded for endangered estuarine/marine fish and invertebrates species (See Table 5). There are no estuarine invertebrate or fish species in any of the counties for the proposed use.

The LOC is exceeded for chronic risk to endangered mammals (Table 4).

The Indiana Bat is the only endangered mammal listed in Indiana. The Indiana Bat inhabits the following counties: Stark, LaPorta, Jasper, St. Joesph, LaGrange, Pulaski, Newton, Porter.

Measures must be taken to ensure the protection of this species from pyridate exposure by contacting the Indiana state endangered species program and/or the U.S. Fish and Wildlife Service.

Since, there are no plant toxicity data available, no plant risk assessment can be done. Therefore, EFED assumes that terrestrial and aquatic non-target plants (including endangered species) may be adversely affected from the labeled use of pyridate.

There is a concern for the following endangered plant species:

<u>Counties</u>	<u>Species</u>
Porter	Pitcher's Thistle

Measures must be taken to ensure the protection of these species from pyridate exposure by contacting the Indiana state endangered species program and/or the U.S. Fish and Wildlife Service.

VII. Recommended Label Modifications

No additional labeling modifications are recommended.

Attachment

SUBJECT: Pyridate Environmental Fate Characteristics and Estimated Ground Water and Surface Water Concentrations Resulting from Proposed Use on Garbanzo Beans (Chemical No. 128834, DP Barcode D223398, Case 287340, ID 6E04667)

FROM: John Simons, Environmental Scientist
Environmental Risk Branch 2
Environmental Fate and Effects Division (7507C)

THROUGH: Elizabeth Leovey, Chief
Environmental Risk Branch 2
Environmental Fate and Effects Division (7507C)

TO: Robert Forrest, Product Manager 21
Minor Use, Inerts & Emergency Response
Registration Division

CONCLUSIONS

Pyridate generally hydrolyzes rapidly to a major degradate, CL-9673, and several minor degradates. CL-9673 is persistent under anaerobic conditions and moderately persistent under aerobic conditions, with CL-9673 K_d values of 0.3 to 3.5 ml/g in four soils. It is also mobile, with computed K_{oc} values for three soils ranging from 30 to 86.5. Some leaching to ground water is predicted from these fate characteristics and the drinking water exposure from the ground water screening model, SCI-GROW, yields a peak estimated environmental concentration (EEC) of 4.4 ppb in ground water. This value may be used for peak and chronic estimates. The fate characteristics also indicate that pyridate would be available for runoff to surface water. The peak GENECC EEC of pyridate in surface water is 97 ppb, and the average 56 day EEC is 75 ppb.

ENVIRONMENTAL FATE

Pyridate hydrolyzes rapidly with half lives of 66.7, 17.8, and 6.8 hours at pH 5, 7, and 9, respectively. The degradate, CL-9673, appears to be stable to hydrolysis with a reported half life of >35 days (>95% remained as CL-9673 after 35 days).

Pyridate does not undergo any significant aqueous or soil photolysis, but is rapidly hydrolyzed to CL-9673, which is in turn readily photolyzed in water with a half life of 3.7 to 14 days and on soil with a half life of 16 days. These half lives indicate that pyridate and its primary degradate will be short lived in the environment when exposed to sunlight. CL-9673 has terrestrial field dissipation half lives of 7-29 days.

In anaerobic conditions, the degradate is persistent with a half life for anaerobic soil metabolism of 330-630 days. The soil partition coefficient (K_d) for CL-9673 is 0.3-3.5, indicating it is not sorbed.

Neither pyridate nor CL-9673 is volatile, with a vapor pressure for pyridate of 7.49×10^{-9} , and a Henry's Constant of 2.49×10^{-9} , meaning pyridate is less volatile than water. A fish study indicated that pyridate bioaccumulates (464 times), but 99% of residues were eliminated in 14 days.

In summary, the data indicate that in terrestrial and aquatic environments, pyridate rapidly hydrolyzes to CL-9673 with half lives usually ≤ 3 days. Although pyridate is also rapidly hydrolyzed under anaerobic soil conditions to CL-9673, CL-9673 is persistent and undergoes very little degradation with half lives from 330-630 days in anaerobic soil conditions. Aerobic half lives of CL-9673 are about 10-30 weeks in soils (incorrectly given as 10-30 days in the EPA one-liner database). CL-9673 is rapidly degraded under the influence of light as indicated by the 14 day half life in the water and 16 day half life in soil. In general, pyridate and its primary degradate, CL-9673, will not persist in aerobic conditions, while CL-9673 will persist in anaerobic conditions.

SURFACE WATER ASSESSMENT:

The GENEEC model was used to estimate surface water concentrations for pyridate. Garbanzo beans (chick peas) were used as the crop of interest. The modeling results indicate that pyridate has the potential to move into surface waters, especially during times of unusually heavy rainfall.

The peak GENEEC estimated environmental concentration (EEC) of pyridate in surface water is 96.72 ppb (Table 1). This estimate is based on a maximum application rate of 0.9 lb ai/acre. The GENEEC values represent upper-bound estimates of the concentrations that might be found in surface water due to pyridate use.

GENEEC (USEPA, 1995) is a screening model designed by the Environmental Fate and Effects Division (EFED) to estimate the concentrations found in surface water for use in ecological risk assessment. As such, it provides upper-bound values on the concentrations that might be found in ecologically sensitive environments because of the use of a pesticide. It was designed to be simple to use and to only require data which is typically available early in the pesticide registration process. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC is hardwired to represent a 10-hectare field immediately adjacent to a 1-hectare pond that is 2 meters deep with no outlet. The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 10% of the applied pesticide into the pond. This amount can be reduced due to degradation on the field and the effects of soil binding in the field. Spray drift is equal to 1 and 5% of the applied rate for ground and aerial spray application, respectively.

GENEEC is not an ideal tool for drinking water risk assessments. Surface water sources of drinking water tend to come from bodies of water that are substantially larger than a 1-hectare pond. Furthermore, GENEEC assumes that essentially the whole basin receives an application of the chemical. In virtually all cases, basins large enough to support a drinking water facility will contain a substantial fraction of area that does not receive the chemical. Furthermore, there is always at least some flow (in a river) or turn over (in a reservoir or lake) of the water so the persistence of the chemical near the drinking water facility is usually over estimated by GENEEC. Given all this, GENEEC does provide an upper bound on the concentration of pesticide that could be found in drinking water and therefore can be appropriately used in screening calculations. If a risk assessment performed using GENEEC output does not exceed the level of concern, then one can be reasonably confident that the risk will also be below the level of concern. However, since GENEEC can substantially overestimate true drinking water concentrations, it will be necessary to refine the GENEEC estimate if the level of concern is exceeded. The input values for GENEEC are listed in Table 2. GENEEC version 1.2 was used for the calculations.

Table 1. GENEEC EECs ($\mu\text{g/L}$) for Pyridate Use on Garbanzo Beans

Crop	Peak GEEC	4 Day GEEC	21 Day GEEC	56 Day GEEC
Garbanzo beans	96.72	95.33	87.90	74.93

Table 2. GENEEC Environmental Fate Input Parameters for Pyridate

DATA	VALUE
Application rate	0.9 lb ai/A (label)
Maximum number of application per year	2 (label)
Interval between applications	20 days (label)
Soil organic carbon coefficient (K _{oc})	3 (lowest computed for three soils) ¹
Soil aerobic metabolism (maximum value)	210 days (261827)
Solubility	1.5 ppm (one liner database)
Aerobic aquatic metabolism half life	75 days(one liner, supplemental study)
Photolysis half life	14.1 days(40939103)

¹ See Table 3 for data used to compute K_{oc} values

GROUND WATER ASSESSMENT

Data indicate that the parent compound, pyridate, does not possess the environmental fate parameters associated with a compound that could leach to ground water. However, the fate parameters of the degradate, CL-9673, do seem to indicate that it has the potential to leach to ground water (K_d of 0.3 - 3.5), especially in soils of low organic matter. An EFED to RD memo of July 6, 1992 requested a prospective ground water study to investigate this possibility, although no such study was conducted as far as known. An earlier review of fate data by EFED (June 29, 1992) concluded that pyridate and CL-9673 probably have limited potential to move downward in the soil profile. This conclusion was substantiated in a field dissipation study in which no detections of CL-9673 were made at depths greater than 12 inches. Although the data shows that CL-9673 is not tightly bound to soil and has the potential to leach, it likely could be degraded by aerobic processes in the soil before it can move appreciably. This was indicated by a study where CL-9673 was initially detected below 6 inches, but no residues were detected after the fifth day following application. In unusual condition such as flooding, where anaerobic conditions existed in the top soil layers for up to 60 days, CL-9673 could persist and possibly leach to ground water or run off to surface water.

Pyridate is not listed in the EPA Pesticides in Ground Water Database, nor is there an EPA MCL or health advisory.

Table 3 shows the input parameter values used in SCI-GROW for pyridate as well as the resulting estimated ground water concentration.

Table 3. SCI-GROW Environmental Fate Input Parameters for Pyridate

Average K_{oc} (l/kg) ¹	64.5
Application rate (lb a.i./acre)	0.9
Number of applications per year	2
Use rate (maximum total/season)	1.8 lb ai/A
Aerobic soil metabolism half-life (days)(average)	105
Relative intrinsic leaching potential	4.9
Estimated groundwater concentration	4.44 ppb

¹ The K_{oc} used as model input was computed from three K_d values for three soils of different organic carbon. The K_d values were 0.37, 2.3, and 0.3 with % organic carbon of 0.48, 2.66, and 1.0, respectively. This gave K_{oc} values of 77, 86.5, and 30, for an average K_{oc} of 64.5. Use of the average K_{oc} value gave an estimated ground water concentration of 4.44 ppb. Use of the median K_{oc} gave an estimated ground water concentration of 3.6 ppb. To be conservative, the average K_{oc} value was used to compute EEC. Note that even though K_{oc} was used in model, no significant correlation (at 95% level) was found between organic carbon and K_d .

EFED estimates a drinking water exposure concentration of 4.44 ppb for pyridate as predicted by SCI-GROW modeling results. There may be exceptional circumstances under which groundwater concentrations could exceed the SCI-GROW estimates. However, such exceptions should be quite rare since the SCI-GROW model is based exclusively on maximum groundwater concentrations from studies conducted at sites and under conditions which are most likely to result in groundwater contamination. The groundwater concentrations generated by SCI-GROW are based on the largest 90-day average recorded during the sampling

period. The concentration (4.44 ppb) can be considered as both the acute and chronic values.

GEENEEC MODEL VERSION 1.2 PRINTOUT

RUN No. 1 FOR pyridate INPUT VALUES

RATE (#/AC) ONE(MULT)	APPLICATIONS NO.-INTERVAL	SOIL KOC	SOLUBILITY (PPM)	% SPRAY INCORP DRIFT DEPTH(IN)
.900(1.743)	2 20	3.0 1.5	1.0	.0

FIELD AND STANDARD POND HALFLIFE VALUES (DAYS)

METABOLIC DAYS UNTIL (FIELD)	HYDROLYSIS RAIN/RUNOFF (POND)	PHOTOLYSIS (POND-EFF)	METABOLIC COMBINED (POND)
210.00	0	N/A 14.10-1730.07	75.00 71.88

GENERIC EECs (IN PPB)

PEAK GEEC	AVERAGE 4 DAY GEEC	AVERAGE 21 DAY GEEC	AVERAGE 56 DAY GEEC
96.72	95.33	87.90	74.93

SCIGROW VERSION 1.0 PRINTOUT

RUN No. 1 FOR PYRIDATE INPUT VALUES

APPL (#/AC) RATE	APPL. URATE NO. (#/AC/YR)	SOIL KOC	SOIL AEROBIC METABOLISM (DAYS)
.900	2	1.800	64.5 105.0

GROUND-WATER SCREENING CONCENTRATIONS IN PPB

4.436610

A= 100.000 B= 69.500 C= 2.000 D= 1.842 RILP= 4.316
F= .392 G= 2.465 URATE= 1.800 GWSC= 4.436610

REFERENCES:

Barrett, M. Proposal For a Method to Determine Screening Concentration Estimates for Drinking Water Derived from Ground Water Studies. EFED/OPP. September 20, 1997.

U.S. Environmental Protection Agency. National Pesticide Survey. Office of Water. OPTS. 1990.

U.S. Environmental Protection Agency. 1992. Pesticides in Ground Water Database - A Compilation of Monitoring Studies: 1971 - 1991. Office of Prevention, Pesticides, and Toxic Substances, EPA 734-12-92-001, September 1992.

U.S. Environmental Protection Agency. 1995. *GENEEC: A Screening Model for Pesticide Environmental Exposure Assessment*. The International Symposium on Water Quality Monitoring, April 2-5 1995. American Society of Agricultural Engineers. p 485.

U.S. Environmental Protection Agency. 1996. Drinking Water Regulations and Health Advisories. USEPA Report. U.S. Government Printing Office, Washington, DC.

Peer reviewed by: William R. Effland, Ph.D.

MEMORANDUM

SUBJECT: Section 18 Emergency Exemption - Use of Pyridate on Garbanzo Beans (Chickpeas) in Washington State to Control Broadleaf Weeds (D244668, PC Code# 128834, ID # 98WA0031)

FROM: Michael Davy, Agronomist
Environmental Risk Branch II
Environmental Fate and Effects Division

THRU: Elizabeth Leovey, Branch Chief
Environmental Risk Branch II
Environmental Fate and Effects Division

TO: Robert Forrest, PM 05,
Minor Use, Inerts & Emergency Response Branch
Registration Division

A. SUMMARY

ERBII/EFED concurs with the proposed emergency use of pyridate on garbanzo beans in Washington to control broadleaf weeds. Pyridate is not expected to pose a threat to ground water, and under normal use pyridate is not expected to reach surface water. In addition, EFED concludes that because of the limited acres to be treated (6,000) and the product to be used (10,800 lbs. ai) the environmental risk is minimal. However, an endangered plant species, Water Howellia, that inhabits Spokane county has been identified as a possible "may effect".

B. SUBMISSION PURPOSE

The State of Washington is requesting an emergency exemption under section 18 of FIFRA to use pyridate on garbanzo beans to control broadleaf weeds. This is the second year this use has been requested. Pyridate is a post-emergence contact herbicide that is currently used in Europe and Asia to control broadleaf and some grassy weeds in a variety of crops. The mode of action is understood to be inhibiting photosynthesis. An EUP was granted by EPA in 1987.

C. USE INFORMATION

Application: By ground equipment only, from April 13 - June 26, 1998 in Central Basin and Walla Walla region of counties; and from May 2 - July 15, 1998 in Palouse area.

Rates: 0.9 lb. a.i. per acre (2 pints of product), two applications per season at least 20 days apart.

Total area: 6,000 acres in Washington.

Total pounds: At the maximum allowable use of 2 applications of 2 pints (0.9 lbs. a.i. per acre) on 6,000 acres, a total of 3,000 gallons of formulated product (10,800 lbs. a.i.) may be used.

D. USE RESTRICTIONS

- 1.) Do not apply by air.
- 2.) Do not apply through any type of irrigation system.
- 3.) Application may not be made within 60 days of harvest.
- 4.) Do not allow livestock to graze on treated fields. Do not feed forage, hay or silage from treated fields to livestock.

E. ENVIRONMENTAL ASSESSMENT

1. Environmental Fate Assessment

Pyridate generally degrades rapidly in the environment to form several minor degradates (unidentified) and one major degradate, CL-9673, which is more stable than the parent.

Pyridate hydrolyzes rapidly with half lives of 66.7, 17.8, and 6.8 hours at pH 5, 7, and 9, respectively. The degradate, CL-9673, is relatively stable to hydrolysis with a reported half life of >35 days (>95% remained as CL-9673 after 35 days).

Pyridate does not undergo any significant aqueous or soil photolysis, but is rapidly hydrolyzed to CL-9376, which is readily photolyzed in water with a half life of 3.7 to 14 days and on soil with a half life of 16 days. These half lives suggest that pyridate and its primary degradate will be short lived in the environment when exposed to sunlight. CL-9376 has a terrestrial field dissipation half life of 7-29 days.

In anaerobic conditions, the degradate is persistent with a half life for anaerobic soil metabolism of 330-630 days. The soil partition coefficient (Kd) for CL-9673 is 0.3-3.5, showing it has the potential to leach to ground water.

Neither pyridate nor CL-9673 is volatile. A fish study showed that pyridate bioaccumulates (464 times), but 99% of residues were eliminated in 14 days.

In summary, the data shows that in terrestrial and aquatic environments, pyridate rapidly hydrolyzes to CL-9673 with half lives usually ≤ 3 days. Although pyridate is also rapidly hydrolyzed under anaerobic soil conditions to CL-9673, CL-9673 is persistent and undergoes very little degradation with half lives from 330-630 days in anaerobic soil conditions. Aerobic half lives of CL-9673 are about 10-30 days in soils. CL-9673 is rapidly degraded under the influence of light as showed by the 14 day half life in the water and 16 day half life in soil. Overall, pyridate and its primarily degradate, CL-9673, will not persist in aerobic conditions, while CL-9673 will persist in anaerobic conditions.

SURFACE WATER ASSESSMENT:

The GENEEC model was used to estimate surface water concentrations for pyridate. Garbanzo beans (chick peas) were used as the crop of interest. The modeling results show that pyridate has the potential to move into surface waters, especially during times of unusually heavy rainfall.

The peak GENEEC estimated environmental concentration (EEC) of pyridate in surface water is 97 ppb (Table 1). This estimate is based on a maximum application rate of 0.9 lb. ai/acre. The GENEEC values represent upper-bound estimates of the concentrations that might be found in surface water due to pyridate use.

GENEEC (USEPA, 1995) is a screening model designed by the Environmental Fate and Effects Division (EFED) to estimate the concentrations found in surface water for use in ecological risk assessment. As such, it provides upper-bound values on the concentrations that might be found in ecologically sensitive environments because of the use of a pesticide. It was designed to be simple to use and to only require data that is typically available early in the pesticide registration process. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC is hardwired to represent a 10-hectare field immediately adjacent to a 1-hectare pond that is 2 meters deep with no outlet. The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 10% of the applied pesticide into the pond. This amount can be reduced due to degradation on the field and the effects of soil binding in the field. Spray drift is equal to 1 and 5% of the applied rate for ground and aerial spray application, respectively.

GENEEC is not an ideal tool for drinking water risk assessments. Surface water sources of drinking water tend to come from bodies of water that are substantially larger than a 1-hectare pond. Furthermore, GENEEC assumes that essentially the whole basin receives an application of the chemical. In virtually all cases, basins large enough to support a drinking water facility will contain a substantial fraction of area that does not receive the chemical. Furthermore, there is always at least some flow (in a river) or turn over (in a reservoir or lake) of the water so the persistence of the chemical near the drinking water facility is usually over estimated by GENEEC. Given all this, GENEEC does provide an upper bound on the concentration of pesticide that could be found in drinking water and therefore can be appropriately used in screening calculations. If a risk assessment performed using GENEEC output does not exceed

the level of concern, then one can be reasonably confident that the risk will also be below the level of concern. However, since GENEEC can substantially overestimate true drinking water concentrations, refining the GENEEC estimate will be necessary if the level of concern is exceeded. The input values for GENEEC are listed in Table 2. GENEEC version 1.2 was used for the calculations.

Table 1. GENEEC EECs ($\mu\text{g/L}$) for Pyridate Use on Garbanzo Beans

Crop	Peak GEEC	4 Day GEEC	21 Day GEEC	56 Day GEEC
Garbanzo beans	97	95	88	75

Table 2. GENEEC Environmental Fate Input Parameters for Pyridate

DATA	VALUE
Application rate	0.9 lb ai/A (label)
Maximum number of application per year	2 (label)
Interval between applications	20 days (label)
Soil organic carbon coefficient (K_{oc})	3 (lowest computed for three soils) ¹
Soil aerobic metabolism (maximum value)	210 days (261827)
Solubility	1.5 ppm (one liner database)
Aerobic aquatic metabolism half life	75 days (one liner, supplemental study)
Photolysis half life	14.1 days (40939103)

¹ See Table 3 for data used to compute K_{oc} values

GROUND WATER ASSESSMENT

Data show that the parent compound, pyridate, does not possess the environmental fate parameters associated with a compound that could leach to ground water. However, the fate parameters of the degradate, CL-9673, do seem to show that it has the potential to leach to ground water (K_d of 0.3 - 3.5), especially in soils of low organic matter. An EFED to RD memo of July 6, 1992 requested a prospective ground water study to investigate this possibility, although no such study was conducted as far as known. An earlier review of fate data by EFED (June 29, 1992) concluded that pyridate and CL-9673 probably have limited potential to move downward in the soil profile. This conclusion was substantiated in a field dissipation study in which no detections of CL-9673 were made at depths greater than 12 inches. Although the data shows that CL-9673 is not tightly bound to soil and has the potential to leach, it likely could be degraded by aerobic processes in the soil before it can move appreciably. This was shown by a study where CL-9673 was initially detected below 6 inches, but no residues were detected after the fifth day following application. In unusual condition such as flooding, where anaerobic conditions existed in the top soil layers for up to 60 days, CL-9673 could persist and possibly leach to ground water or run off to surface water.

Pyridate is not listed in the EPA Pesticides in Ground Water Database, nor is there an EPA MCL or health advisory.

Table 3 shows the input parameter values used in SCI-GROW for pyridate and the resulting estimated ground water concentration.

Table 3. SCI-GROW Environmental Fate Input Parameters for Pyridate

Average K_{oc} (l/kg) ¹	64.5
Application rate (lb a.i./acre)	0.9
Number of applications per year	2
Use rate (maximum total/season)	1.8 lb ai/A
Aerobic soil metabolism half-life (days)(average)	105
Relative intrinsic leaching potential	4.9
Estimated groundwater concentration	4.44 ppb

¹ The K_{oc} used as model input was computed from three K_d values for three soils of different organic carbon. The K_d values were 0.37, 2.3, and 0.3 with % organic carbon of 0.48, 2.66, and 1.0, respectively. This gave K_{oc} values of 77,86.5, and 30, for an average K_{oc} of 64.5. Use of the average K_{oc} value gave an estimated ground water concentration of 4.44 ppb. Use of the median K_{oc} gave an estimated ground water concentration of 3.6 ppb. To be conservative, the average K_{oc} value was used to compute EEC. Note that even though K_{oc} was used in model, no significant correlation (at 95% level) was found between organic carbon and K_d .

EFED estimates a drinking water exposure concentration of 4.44 ppb for pyridate as predicted by SCI-GROW modeling results. There may be exceptional circumstances under which groundwater concentrations could exceed the SCI-GROW estimates. However, such exceptions should be quite rare since the SCI-GROW model is based exclusively on maximum groundwater concentrations from studies conducted at sites and under conditions that are most likely to result in groundwater contamination. The groundwater concentrations generated by SCI-GROW are based on the largest 90-day average recorded during the sampling period. The concentration (4.44 ppb) can be considered as both the acute and chronic values.

2. Ecological Risk Assessment

a. Toxicity Data

Pyridate is practically nontoxic to birds on a dietary basis ($LC_{50} > 5000$ ppm for mallard and bobwhite), but slightly toxic on an acute oral basis ($LD_{50} > 1269$ and 1505 mg/kg for bobwhite). Avian Reproduction studies show NOEL to be 1600 ppm for bobwhite and 640 ppm for mallard.

HED's Mammalian studies show that pyridate is practically nontoxic ($LD_{50} = 3544$ mg/kg). The 3-generation rat study show the NOEL = 216 ppm.

Pyridate is moderately toxic to freshwater fish ($LC_{50} > 1.2$ ppm) and aquatic invertebrates ($LC_{50} = 1.08$ ppm), highly toxic to estuarine fish and clams ($LC_{50} > 0.3$ and 0.145 ppm,

respectively), and moderately toxic to shrimp ($LC_{50} = 3.8$ ppm). The only toxicity data available on the primary degradate, CL-9673, is an $LC_{50} = 26$ ppm for an aquatic invertebrate, *Daphnia*.

There are no data available to provide a risk assessment to non-target plants.

b. Risk Assessment

Aquatic

The Risk Quotients (RQ) are derived by dividing the exposure value by the toxicity value. To determine aquatic exposure, a computer tier I model, GENEEC, was used. The estimated peak concentrations in an aquatic environment would be 97 ppb.

The aquatic Risk Quotients (RQ) are as follows:

Fish	0.08
Aquatic invertebrates	0.09
Estuarine fish	0.32
Shrimp	0.03
Oysters (Clams)	0.67

The freshwater fish LC_{50} cannot be determined at the solubility level. Therefore, minimal risk is assumed for fish. The Level of Concern (LOC) has been exceeded for endangered species for freshwater invertebrates, estuarine fish and clams/mussels. The LOC has also been exceeded for consideration as a restricted use candidate for estuarine fish and clams/mussels.

Although the LOC has been exceeded for restricted use and endangered species, the LOC exceedances are uncertain for the following reasons:

- The GENEEC-run concentrations may be more reflective of the pyridate degradate, CL-9673, since the parent pyridate tends to degrade to CL-9673 rapidly. Toxicity data for CL-9673 are not available for freshwater fish and estuarine species.
- The aquatic toxicity tests were conducted under static conditions. The static conditions may have initial toxicity of the parent pyridate and later have toxicity of the degradate, CL-9673. It is uncertain what chemical the organisms may have been exposed to for the duration of the time. CL-9673 toxicity data on *Daphnia* show that CL-9673 may be less toxic than the parent pyridate on aquatic organisms however, this is uncertain due to lack of toxicity data on CL-9673.
- Pyridate is insoluble in water at approximately 1.5 ppm. The LC_{50} for rainbow trout is greater than the highest concentration tested. About 40% of the fish were dead at the highest concentration. The bluegill study showed no mortality at the highest concentration tested (2.1 ppm). Since the LOC for freshwater fish is very marginal, it

is the opinion of the reviewer that minimal risk can be expected.

- Pyridate is insoluble in water at approximately 1.5 ppm. The LC_{50} for estuarine fish is greater than the highest concentration tested. There are no mortalities found at the highest concentration tested in estuarine fish study. This lack of mortality may show that the LOC exceedances may be much lower than estimated.

There are no chronic data available to provide chronic risk assessment for aquatic species.

Terrestrial

The exposure for terrestrial animals is usually determined by the Kenaga/Fletcher nomogram. The highest terrestrial residue anticipated is determined by multiplying the residues found on short grass (240 ppm) after application of 1 lb ai/A with the application rate (0.9×2 applications) resulting in 432 ppm. The RQ is then divided by the toxicity endpoint. The following RQ's were calculated for terrestrial animals:

Birds	0.09
Mammals	0.01

The terrestrial chronic RQ are as follows:

Birds	0.68
Mammals	0.32

There are no LOC exceedances for the terrestrial animals.

Plants

Since there are no plant toxicity data available, no plant risk assessment can be done. Therefore, a default assumption is that terrestrial and aquatic non-target plants (including endangered species) will be adversely affected from the labeled use of pyridate.

Endangered Species

The following endangered fish species may inhabit counties where pyridate is to be used on chickpeas:

Chinook Salmon (Snake River), Snake River Sockeye Salmon, Steelhead (Upper Columbia River population), and Bull Trout (Columbia River population).

After consulting with OPP's Endangered Species Protection Program, it was agreed that the endangered fish species will not be affected by the labeled use of pyridate because of the very low LOC exceedances for endangered fish species and the streams and rivers where these species are found are rapid and large. The exposure of these fish species to pyridate will not

be enough to warrant a concern.

However, there is a concern for the endangered plant species, Water Howellia, in Spokane county. Measures must be taken to ensure the protection of this species in Spokane county from pyridate by contacting Washington state endangered species program and/or the U.S. Fish and Wildlife Service.

F. Ground Water Impact

Data show that the parent compound, pyridate, does not possess the environmental fate parameters associated with a compound that could leach to ground water. However, the fate parameters of the degradate, CL-9673, do seem to show that it has the potential to leach to ground water (K_d of 0.3 - 3.5), especially in soils of low organic matter. An EFED to RD memo of July 6, 1992, requested a prospective ground water study to investigate this possibility, although no such study was conducted as far as known. An earlier review of fate data by EFED (June 29, 1992) concluded that pyridate and CL-9673 probably have limited potential to move downward in the soil profile. This conclusion was substantiated in a field dissipation study in which no detections of CL-9673 were made at depths greater than 12 inches. Although the data shows that CL-9673 is not tightly bound to soil and has the potential to leach, it is likely it will be degraded by aerobic processes in the soil before it can move appreciably. This was substantiated by a study where CL-9673 was initially detected below 6 inches, but no residues were detected after the fifth day following application. In unusual condition such as flooding, where anaerobic conditions existed in the top soil layers for up to 60 days, CL-9673 could persist and possibly leach to ground water.

G. Surface Water Impact

Available data show that pyridate and its primary degradate degrade rapidly by hydrolyses and photolysis and would not be expected to create a surface water contamination problem. However, if run-off were rapid, taking less time than the aqueous photolysis half life of up to 14 days, such as following a heavy rain, and CL-9673 was discharged to surface water with anaerobic conditions, it then could persist for a significant length of time of 1.5 to 2.5 years. (An anaerobic aquatic half life is not known, but can be estimated from the anaerobic soil metabolism value to be 1.5 to 2.5 years).

Peer reviewed by:

GENEEC MODEL VERSION 1.2 PRINTOUT

RUN No. 1 FOR pyridate INPUT VALUES

RATE (#/AC)	APPLICATIONS	SOIL	SOLUBILITY	% SPRAY INCORP
ONE(MULT)	NO.-INTERVAL	KOC	(PPM)	DRIFT DEPTH(IN)
.900(1.743)	2 20	3.0 1.5	1.0	.0

FIELD AND STANDARD POND HALFLIFE VALUES (DAYS)

METABOLIC DAYS UNTIL HYDROLYSIS (FIELD)	PHOTOLYSIS RAIN/RUNOFF (POND)	METABOLIC COMBINED (POND-EFF)	(POND)
210.00	0	N/A	14.10- 1730.07 75.00 71.88

GENERIC EECs (IN PPB)

PEAK GEEC	AVERAGE 4 DAY GEEC	AVERAGE 21 DAY GEEC	AVERAGE 56 DAY GEEC
96.72	95.33	87.90	74.93

SCIGROW VERSION 1.0 PRINTOUT

RUN No. 1 FOR PYRIDATE INPUT VALUES

APPL (#/AC)	APPL. URATE	SOIL	SOIL AEROBIC
RATE	NO. (#/AC/YR)	KOC	METABOLISM (DAYS)
.900	2	1.800	64.5 105.0

GROUND-WATER SCREENING CONCENTRATIONS IN PPB